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Metallic alloys suitable for YBCO melt-texturing at low temperature

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Ag–Au–Pd alloys, having a gradient in the concentration of the elements (called diffusion alloys), were investigated in order to find homogeneous alloys suitable for melt-processing of YBCO superconductor. Interface aspects between the superconductor and diffusion alloys and composition profiles of the diffusion alloys after melt texturing are presented. The results obtained with the diffusion alloy led to the development of new ternary homogeneous Ag–Au–Pd alloys of composition (at %) Ag–(18–23)Au–(2–10)Pd. The interface between homogeneous alloys and the YBCO superconductor after melt-processing was characterized and the resistivity–temperature curve obtained with electrical contacts on the metallic part of the composite is shown.

1. Introduction

For electrotechnical applications such as in power transmission, energy storage, generators, etc., high-temperature superconductor (HTSC) materials need to be shaped into composite multifilamentary wires or tapes containing both the superconductor and a metal. The high thermal and electrical conductivity of the metallic component in the tape or wire composites enhance the cryogenic stability of the superconductor component against destruction caused by a localized loss of superconductivity. In addition, the metal–superconductor composite is stronger than the superconductor oxide alone. However, many investigations [1–5] have shown that most metals, platinum and palladium included, interact with the superconductor during high-temperature processing, degrading its superconducting properties.

Silver and gold have been found to have either no effect or a benign effect on the superconducting properties of HTSC materials. Silver is relatively inexpensive compared to gold and could be an economically acceptable material for use in superconducting composite wires or tapes, but its low melting point of 960 °C is a limitation when melt-texturing processes for YBCO superconductors are considered. Recently, Porter *et al.* [2] have reported evidence of reactions between Au–5Pd alloy and YBCO. They suggested that copper is more stable in gold than in YBCO and migrates from the superconductor to the alloy. For Ag–Pd alloys, they also found that the reactivity between the alloy and the peritectic YBCO liquid decreased as the palladium concentration increased, the least reactive alloy corresponding to Ag–70Pd.

In this work, we report on an investigation of the interactions between Ag–Au–Pd alloys containing compositional gradients and the liquid phases formed by the decomposition of YBCO in air, at 995 and 1030 °C. The aim of the present investigation was to find ternary Ag–Au–Pd alloys inert to Y–Ba–Cu–O liquids and thus suitable for use in metal–superconducting composites.

2. Experimental procedure

An Ag–Au–Pd alloy having a gradient in the concentration of the elements (called diffusion alloy) was made by heating superimposed foils of silver, gold and 70Ag–30Pd alloy, as illustrated in Fig. 1. The diffusion alloy was obtained by first annealing the superimposed foils in a furnace preheated to 947 °C for 15 h in air. The treated foils were then given a second diffusion anneal at 1000 °C for 30 min with an intermediate pressing step. It is important to note that the measured melting point of the silver foil used was between 945 and 950 °C in air. Subsequently, the diffusion alloy was placed on a nickel substrate and a $25 \times 6 \times 1$ mm^3 superconducting bar was deposited on the silver-rich side of the diffusion alloy and partially melt-textured. Two different heating schedules were used for melt processing. First, the composite was placed in a tube furnace at 995 °C for 45 min, cooled to 940 °C in 6 h and then slowly cooled to 400 °C in 45 h. The second schedule consisted in placing the composite in the furnace at 1030 °C for 30 min, rapidly cooling to 1010 °C, cooling to 930 °C in 24 h and then slowly cooling to 400 °C in 40 h.

After melt-processing the composite YBCO–diffusion alloy, scanning electron microscope (SEM) and quantitative energy-dispersive X-ray spectroscopy (EDS) were used to determine composition profiles in the alloy side of the tape, as well as to identify the presence of reaction layers at the interface alloy/YBCO.

The Ag–Au–Pd alloy composition that showed no interaction with the Y–Ba–Cu–O liquid and two other close compositions were selected for the preparation

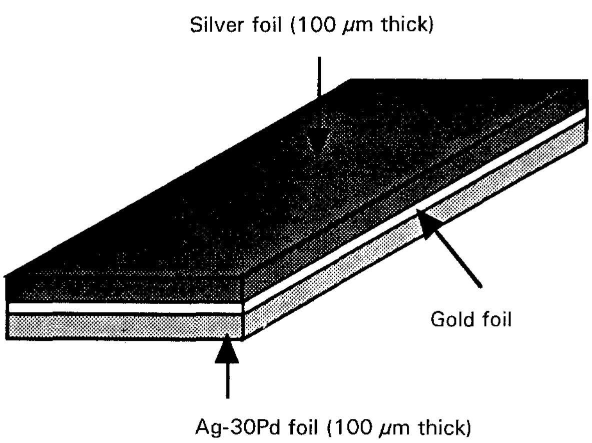

Figure 1 Schematic superposition of silver, gold and silver–palladium foils before heating to obtain the diffusion alloy.

TABLE I Compositions of the homogeneous alloys

Alloy	Composition (at %)
1	Ag–23Au–6Pd
2	Ag–18Au–8Pd
3	Ag–22Au–8Pd

of homogeneous Ag–Au–Pd alloys. The selected alloy compositions are listed in Table I. The alloys were fabricated by melting strips of silver, gold and Ag–30Pd in appropriate ratios. Alloy homogenization was achieved by cold working the resulting ingots three times with an intermediate annealing step. This process resulted in strips about 100 μm thick. These strips were used for making three composite YBCO–(Ag–Au–Pd) samples. First, a bulk sample consisting of a superconducting bar of dimensions 25 × 6 × 1 mm^3 was deposited on Ag–Au–Pd alloy strips. The preparation of the second sample consisted in sandwiching a mixture of $YBa_2Cu_3O_x$ (Y123), Y_2BaCuO_5 (Y211) and Ag_2O between two strips of the same Ag–Au–Pd homogeneous alloy. This was done by depositing a slurry of the ceramic components on to one strip, and then pressing the other strip against the ceramic layer to form the sandwich. Y211 was added in order to favour the recrystallization of the Y123 phase during cooling in the partially molten state, while Ag_2O was added to favour the formation of the liquid and to minimize crack formation. A third sample was made by depositing the slurry on to both faces of a metallic alloy strip. The results obtained with this third sample are presented elsewhere [6].

The procedure employed for melt-texturing the first and second kind of sample consisted typically in introducing the composite strips into a tube furnace pre-heated to 1015 °C, holding at this temperature for 30 min, cooling slowly to 900 °C in 40 h and finally cooling to 500 °C in 15 h. The melt-processed strips were then annealed in oxygen to restore superconductivity.

SEM and a quantitative EDS programme using standards were also used to characterize the interface between the oxide and the homogeneous alloys. The resistivity of metal–superconductor composites and transport J_c at 77 K in zero applied field were obtained with a conventional four-probe technique. The current and voltage leads were soldered directly on to the metallic part of the composites. J_c values were determined using a criterion of 2 μV cm^{-1}.

3. Results

3.1. Diffusion alloys

Fig. 2 shows the composition profile of the diffusion alloys following the crystallization process at both 995 and 1030 °C. After the treatment at 995 °C, the composition (at %) of the alloy near the interface with the superconductor was Ag–20Au–(2–5)Pd. Fig. 3 shows that no reaction occurred between the oxide and the metallic foil. However, a gap between the metal and the YBCO superconductor was present in some locations along the interface.

Different regions were found along the interface metal–YBCO after crystallization at 1030 °C. Unreacted regions were found whenever a gap was present between the oxide and the silver alloy, as shown in Fig. 4. The concentration of palladium in the alloy at the interface with the superconductor was lower when no reaction occurred, i.e. 10 at % compared to 10.5–12.5 at % when a reaction area was present in the oxide layer. This suggested that the diffusion of palladium is more important if the YBCO superconductor is in contact with the alloy. This is probably related to the

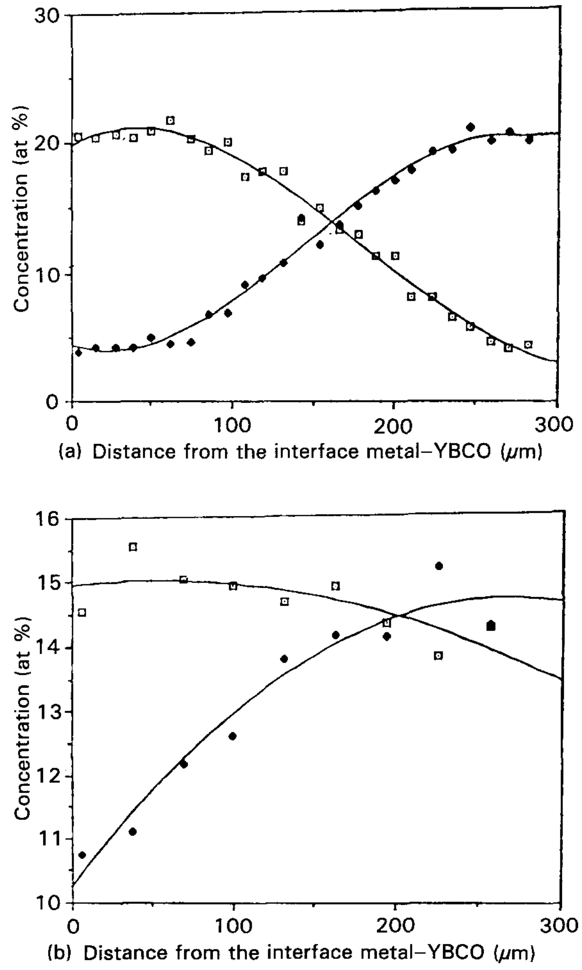

Figure 2 Composition profile of the diffusion alloy after crystallization processes at (a) 995 °C and (b) 1030 °C. (□) Gold, (♦) palladium.

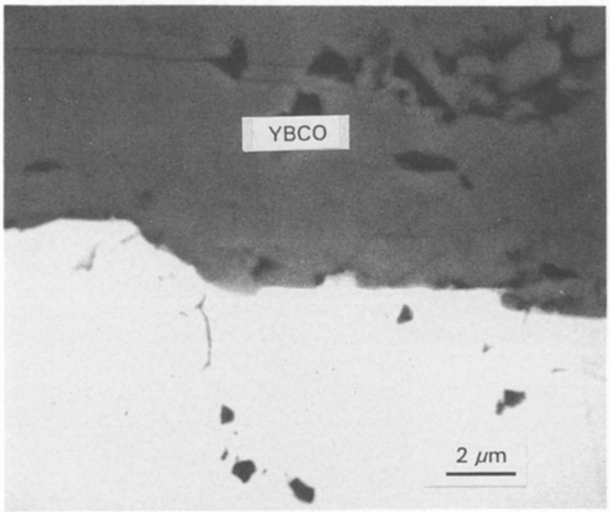

Figure 3 The interface between the superconductor and the diffusion alloy after heat treatment at 995 °C.

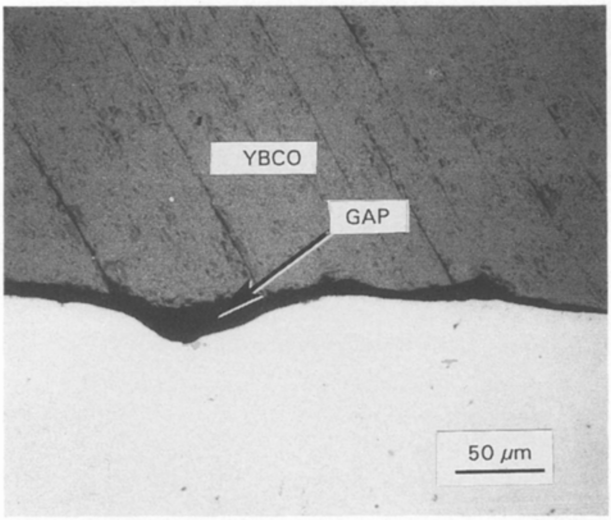

Figure 4 The presence of a gap between the superconductor and the silver diffusion alloy after heat treatment at 1030 °C. The gap is associated with unreacted zones.

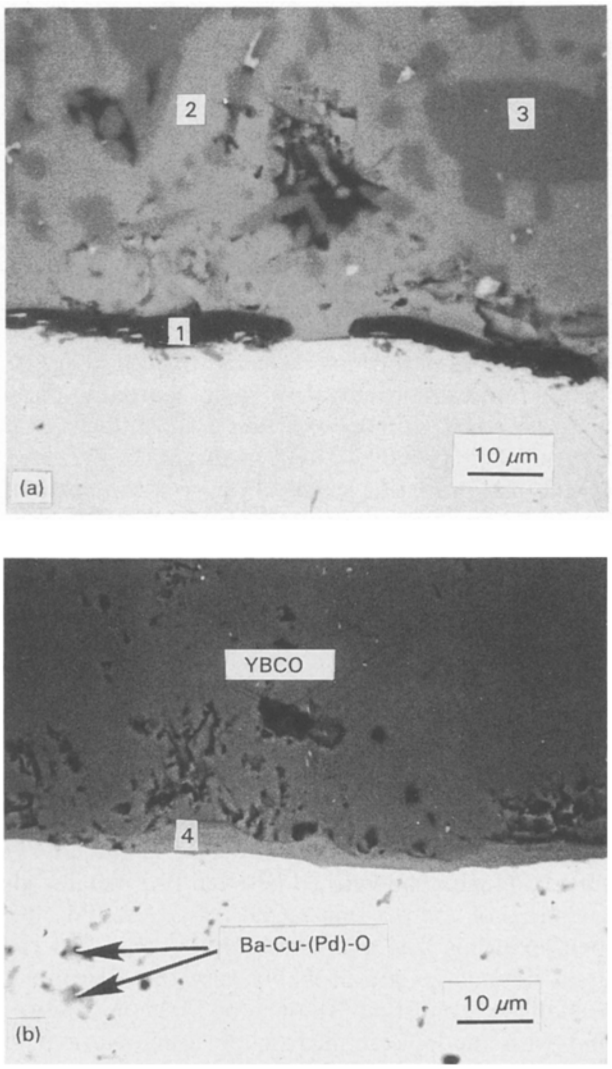

Figure 5 The interface between the silver diffusion alloy and the superconductor after the crystallization process at 1030 °C. (a) CuO or (b) 8Pd–37Ba–55Cu–O is directly in contact with the metallic alloy. In (a), Y_2BaCuO_5 (3) and typically 50Ba–40Cu–8Pd–2Ni–O (2) are also observed at the interface YBCO/metallic alloy.

formation of a complex Ba–Cu–Pd oxide [1] by reaction of palladium with the Ba–Cu–O liquid, which preferentially removed palladium from the alloy. Porter *et al.* [2] have also observed a gap along the interface between the superconductor and a foil of Ag–70Pd after firing at 1100 °C. The existence of such a gap may explain the absence of interactions between the oxide and the metal in their study, as indeed observed in the present work (Fig. 4). Fig. 5a and b show two typical reacted regions in the superconductor side of the interface after crystallization at 1030 °C. SEM metallographs showed that the alloy was slightly porous and was infiltrated by the Ba–Cu–(Pd)–O liquid during the high-temperature step (see Fig. 5b). In the reacted area, thin layers of CuO (1 in Fig. 5a) or 8Pd–37Ba–55Cu–O (4 in Fig. 5b) are directly in contact with the silver alloy. These compositions are semi-quantitative because the diameter of the electron beam is similar to the thickness of the thin layers that were analysed. In Fig. 5a, the reaction zone over the thin CuO layer is composed of Y_2BaCuO_5 (3) and a phase typically composed of 50Ba–40Cu–8Pd–2Ni–O (2). The nickel in the latter phase was provided by the nickel substrate which supported the silver alloy and the superconductor oxide during the melt-processing. In reacted regions, where an intimate contact between the 211 phase and Ba–Cu–Pd–O existed, the 123 superconducting phase did not form during processing. This suggested that the presence of palladium in non-negligible concentrations in the Ba–Cu–O liquid modifies the equilibrium in the Y–Ba–Cu–O system. In the present experiments, this concentration was around 3 at %. This behaviour was observed in all samples containing reacted areas. The presence of a gap or CuO or a complex Ba–Cu–Pd–O between the superconductor and the metallic alloy must be avoided because it prevents good electrical contact between the metal and the superconductor, limiting the cryogenic stability of the superconducting body if a local loss of superconductivity occurs. It is important to note that these reactions at the interface were not detrimental to the superconducting properties of the 123 phase. In fact, palladium was not detected in the 123 phase and the transition temperature, T_c, was 92 K even in samples where interfacial reactions were observed.

3.2. Homogeneous alloys

The results obtained with the diffusion alloy suggested that homogeneous alloys with palladium concentration between 2% and 10% could be suitable for YBCO melt-processing, the gold content of the alloy may be chosen according to the desired melting point. Taking into account that many workers [7–11], using different types of precursors, have obtained high values of critical current density by partially melt-texturing their samples between 1040 and 1000 °C instead of 1100–1200 °C used in the MTG [12] and QMG [13] processes, a typical range of composition would be Ag–20Au–(2–10)Pd (at %). In order to confirm the results observed in the diffusion alloys, three homogeneous alloys have been made (see Table I). Preliminary results for melt-textured YBCO/alloy composites with two homogeneous alloys are shown in Figs 6–8.

Fig. 6 shows the interface between a homogeneous alloy of composition (at %) Ag–22Au–8Pd and a bulk sample of YBCO after melt-texturing process from 1015 °C in air. No reaction was observed at the interface. Fig. 7 shows the microstructure of the YBCO superconductor sandwiched between two metallic alloy strips of composition (at %) Ag–23Au–6Pd after melt-texturing. The microstructure is dense and the grain boundaries are probably very thin because it was difficult to distinguish them by SEM (not shown) and with the optical microscope using Normarski technique (Fig. 7). In addition, it contains fine 211 particles with dimensions ranging between 0.5 and 8 μm. As demonstrated by many groups, the presence of fine 211 particles in 123 superconducting grains is favourable to reaching high critical current density [14–17]. However, the microstructure is composed by many domains of aligned grains. Some microcracks perpendicular to the tape axis were also observed, as was the occasional segregation of CuO. These microstructural features are limiting factors for the achievement of high J_c in melt-processed samples. The formation of microcracks may probably be avoided by better processing control.

Fig. 8 shows a resistivity curve typical of these composites. The transition temperature, T_c, was 89 K for the sandwiched superconductors and 92 K for the remaining ones. Considering that electrical contacts were made to the metallic part of the composite, the resistivity curve indicates that current flows easily from the metal to the superconductor at the transition temperature, T_c. These preliminary results are promising, as there is no reaction between the two components during melt-texturing. The transport critical current density, J_c, obtained with composite tapes having the superconductor sandwiched between two metallic foils varied from 600–1500 A cm^{-2}. As mentioned above, many factors may be responsible for these low J_cs. Among these, an important one is the presence of high-angle grain boundaries [18]. Owing to anisotropic conductivity of the YBCO superconductor, it is necessary to align the *a–b* plane along the sample length. Boundaries between domains act as electrical weak links limiting the current-carrying capability of the samples [18]. Another important factor might be the degree of oxygenation in the superconductor. In fact, it is well known that good superconducting properties are obtained when the oxygen level, *x*, in $YBa_2Cu_3O_x$ is close to 7. Also, the diffusion rate of the oxygen into dense Y123 oxide is very low [19]. In the present case, the oxygenation period before observing the complete superconducting transition with the

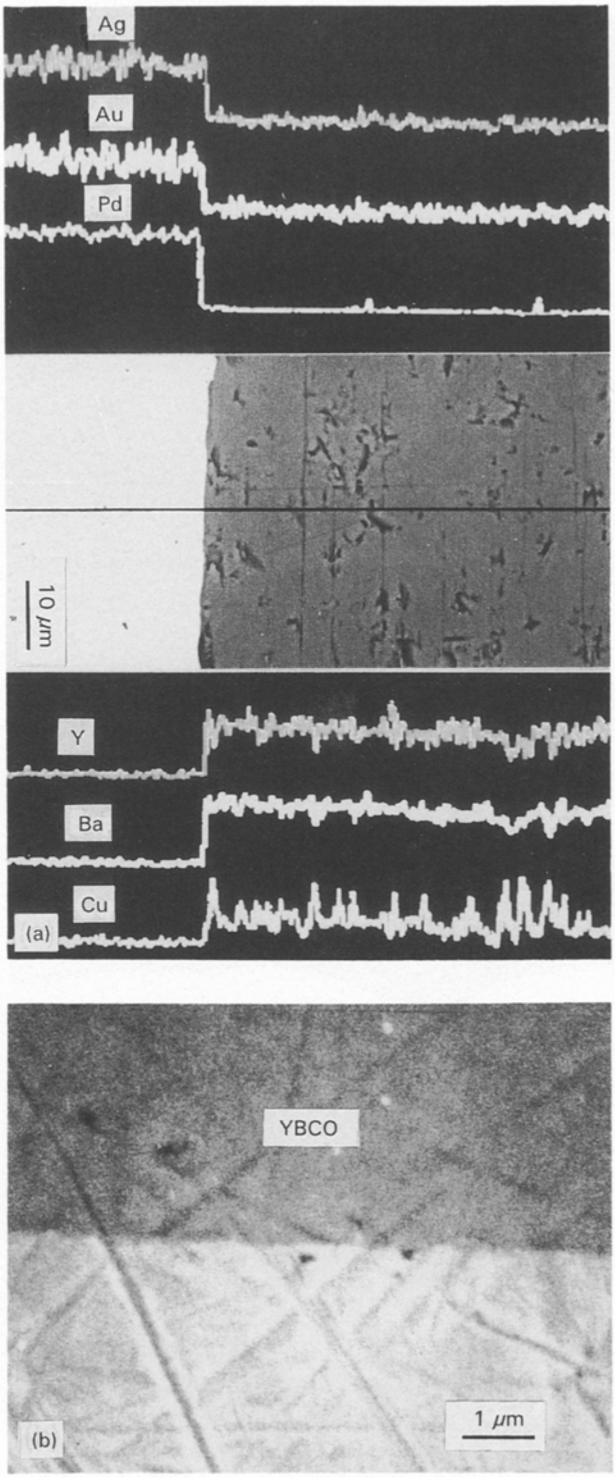

Figure 6 (a) The interface between the homogeneous alloy of composition (at %) 70Ag–22Au–8Pd and the superconductor (Y123). No reaction was observed after the melt-crystallization process starting at 1015 °C in air. (b) Magnification of the interface.

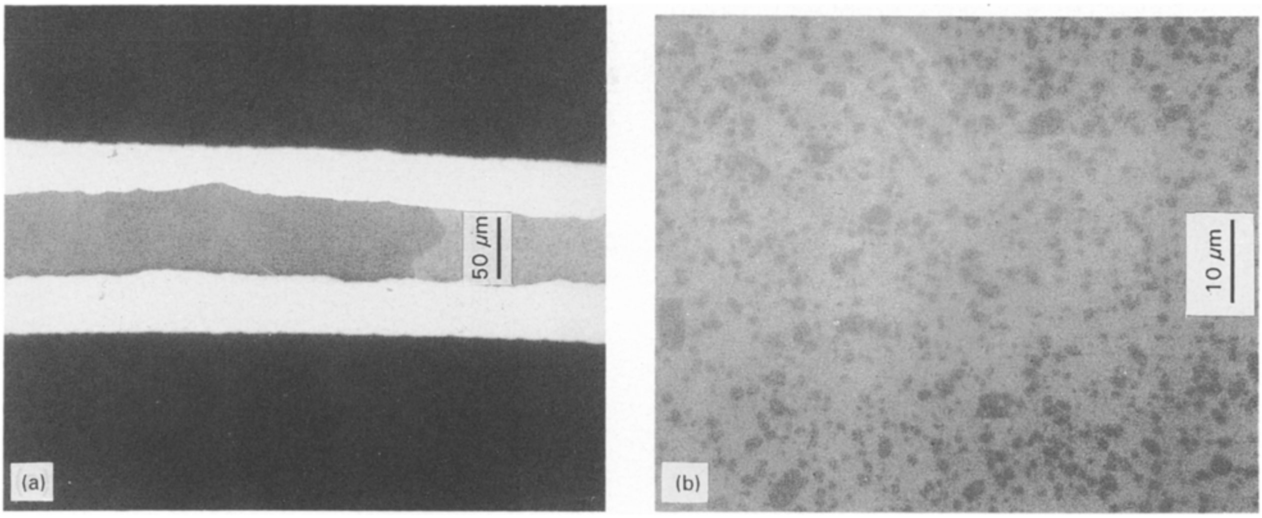

Figure 7 (a) General microstructure of the YBCO/Ag–23Au–6Pd composite and (b) higher magnification of this microstructure showing the distribution and size of 211 inclusions. These figures were obtained using an optical microscope with Normarski technique.

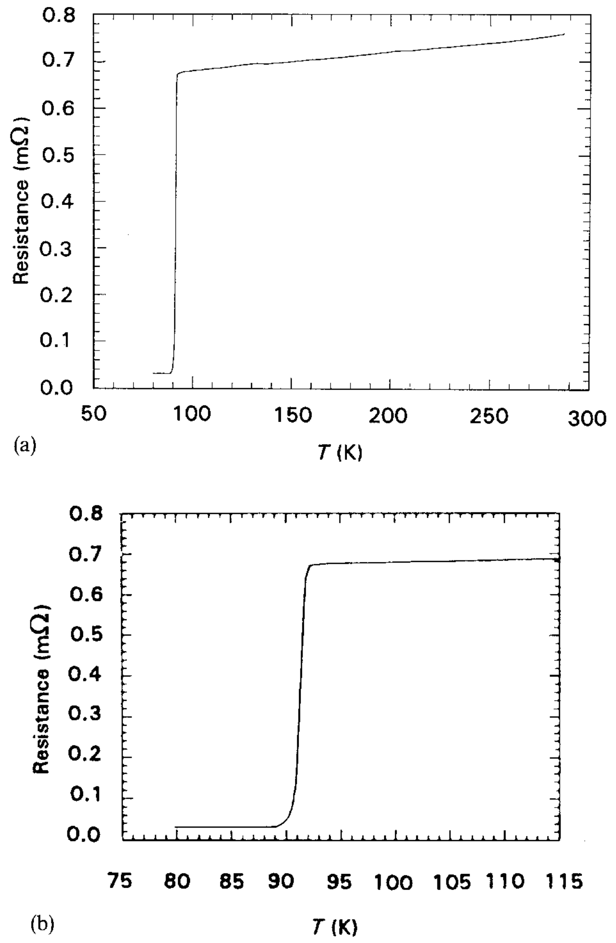

Figure 8 (a, b) Resistance–temperature measurements performed on a composite metal/YBCO superconductor with the electrodes applied on to the metallic part of the composite.

sandwiched sample (Fig. 7) was over 100 h. This is probably due to a very dense microstructure and the fact that the YBCO was partially cladded. Thus, it is possible that the sample core was not well oxygenated and did not contribute to current transport [19]. This hypothesis has not been verified in the present work. In order to facilitate the oxygenation of the superconductor sandwiched between two metallic foils, it is possible to introduce some porosities during melt-processing owing to the modification of the precursors [20].

4. Conclusions

1. New Ag–Au–Pd ternary alloys have been developed that are compatible with Y–Ba–Cu–O liquids. These alloys may be employed in the fabrication of metal/YBCO superconductor composites by melt processing at temperatures above 1000 °C.
2. To avoid reaction of the alloys to Ba–Cu–O liquids, the maximum concentration of palladium may not exceed 10%.
3. It has been observed that 3% Pd and more in the Ba–Cu–O liquid, prevented the formation of the 123 superconducting phase.
4. There is a good electrical contact between the YBCO superconductor and the metallic alloy. That is important for cryogenic stabilization of the superconductor in electrotechnical devices.

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